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THERMODYNAMICS AND PHENOMENOLOGICAL NUCLEATION THEORIES

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Phenomenological nucleation theories are considered from the viewpoint of Gibbs' surface thermodynamics. We point out, in defining the critical nucleus, that it is important to make a distinction between the number of molecules enclosed by the surface of tension and the excess number of molecules over the uniform vapor phase. We show that the Kelvin equation should be employed in determining the size of the critical nucleus even if the nucleus free energy contains a size-dependent surface energy term. Furthermore, we make use of the fact that the classical form of Kelvin equation (containing the surface tension of a flat interfact) predicts the equimolar radius of the critical nucleus well down to nuclei of about 40 molecules, and derive a new equation for the size-dependent surface tension that differs from the Tolman relation. Density functional calculations support the new formula.

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